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(54) **Title:** TI-PILLARED CLAY BASED VANDIA CATALYST AND PROCESS FOR PREPARATION

(57) **Abstract:** This invention relates to a process for the preparation of highly active and selective ammoxidation catalyst using a complex metal oxide containing P, V and Mo supported on Ti-PILC which process involves heating on water bath a vanadium source with oxalic acid in the presence of water to form vanadyl oxalate; adding a source of phosphorous and a source of Mo and Ti-PILC and heating the resultant mixture in the presence of air at a temperature in the range of 110-450°C for a period in the range of 15 to 35 h and the use of said ammoxidation catalyst in the preparation of heteroaromatic nitriles from methyl pyridines which comprises passing as a reactant stream a gaseous mixture comprising, a methyl substituted pyridine, ammonia and oxygen (air) over the fixed bed ammoxidation catalyst at a temperature of about 350 - 450°C.

TI-PILLARED CLAY BASED VANDIA CATALYST AND PROCESS FOR PREPARATION

Field of the invention

The invention relates to a pillared clay based vanadia catalyst. The present invention also relates to a process for the preparation of vanadia based catalyst supported on titanium-pillared clay useful for producing heteroaromatic nitriles. The present invention also relates to a process for the preparation of pillared clay based vanadia catalyst useful for production of nicotinonitrile (3-cyanopyridine) by ammoxidation of 3-picoline and to the use thereof for the production of 3-cyanopyridine.

Background of the invention

The present invention finds its usage in preparing valuable intermediates for the preparation of corresponding amides, which are used in pharmaceuticals. 3-cyano-pyridine is used in the preparation of niacin, used for the treatment of pellagra. Many drugs based on niacin have curative effects such as lowering the limit of cholesterol and free fatty acids in blood, stimulation of the respiratory apparatus, antispasmodic and anti-rheumatic action e.g. the antispasmodic lyspamin and coramine or Nikethamide and Bilamid used in treating infections of gallbladder or bile duct.

Reference is made to US Patent 5,614,453 which relates to acid catalyzed chemical conversion processes, such as hydrocarbon conversion processes, and to the catalysts and catalyst supports used in such processes. The invention is particularly concerned with catalyst supports containing a combination of zeolite Beta and a pillared clay, catalysts comprising such supports and the use of such catalysts in hydrocarbon conversion processes, particularly hydrocracking. There is no mention about conversion of 3-picoline. Reference is also made to US Patents 2,510,605, 2,839,535 and 2,861,999 wherein the catalysts based on vanadium, molybdenum and phosphorous on activated alumina has been described. However, the yields of nicotinonitrile and isonicotinonitrile were in the range of 60 to 70 %. Reference is also made to US Patent 3981879 wherein catalysts based on vanadium, molybdenum, phosphorous oxides and tin oxide over pumice have been described which gives 90% selectivity at 76% conversion. Reference is also made to Japanese Patent 19706 wherein a catalyst has been disclosed, comprising of antimony oxide, vanadium oxide containing a metal from group (iron, copper, titanium, cobalt, manganese and nickel with high selectivity but it deactivates due to reduction by ammonia.

Pillared clays are typically prepared by reacting a smectite clay such as montmorillonite, saponite, hectorite, and beidellite with a pillaring agent or propping agent to

form a flocculated reaction product which is subsequently dried to convert the pillaring agent into inorganic metal oxide clusters which form the pillars which prop apart the layers of the clay. The X-ray diffraction pattern of a pillared clay normally contains a distinct first order reflection which is indicative of a well ordered, long range, face-to-face orientation of the clay platelets.

Prior art search for a process for preparation of titanium based pillared clay catalyst for conversion of 3-picoline to 3-cyanopyridine has been made based on literature survey and patent databases, which did not yield any relevant references.

Objects of the invention

The main object of the present invention is to provide a process for the preparation of a catalyst supported on titanium-pillared clay useful for producing heteroaromatic nitriles.

Another object of the present invention is to provide a process for the preparation of pillared clay based vanadia catalyst useful for production of nicotinonitrile (3-cyanopyridine) by ammoxidation of 3-picoline.

Yet another object of the present invention is to convert 3-picoline into nicotinonitrile in a single step reaction between 3-picoline, ammonia and air.

Still another object of the present invention is to provide a process for preparing 3-cyano pyridine in high yield (>90%).

Summary of the invention

Accordingly the present invention provides a pillared clay based vanadia catalyst useful for the conversion of 3-picoline to 3-cyanopyridine, said catalyst comprising vanadium, phosphorous and molybdenum on a Ti-pillared clay support.

In one embodiment of the invention, the clay is pillared with polyoxymetal cations of titanium and has titania clusters as the pillars between the layers.

In another embodiment of the invention, the clay is selected from a single smectite clay and mixed layer smectite clays.

In another embodiment of the invention, the single smectite clay comprises montmorillonite clay.

In another embodiment of the invention, the mixed layered smectite clay is selected from rectorite and paragonite.

In another embodiment, the pillared clay contains a homogeneous distribution of pillars in the interlayered spaces thereof forming an array of rectangular openings or pores of a size in the range of 7 to 20 Angstroms high and between 8 and 20 Angstroms wide, enabling the pillared clay to perform like a two-dimensional crystalline molecular sieve.

In still another embodiment of the invention the ratio of the compounds of vanadium, molybdenum, phosphorous over titanium pillared clay in the catalyst is in a ratio ranging between 1.0: 2.5: 0.5: 20 - 1.0: 30: 1.5: 50.

In a further embodiment of the invention, the pillared clay contains one or more rare earth elements selected from cerium, lanthanum and a mixture thereof.

The present invention also relates to a process for the preparation of a pillared clay based vandia catalyst comprising first preparing vanadyl oxalate by heating a vanadium rich compound on a water bath followed by addition of oxalic acid till the colour of the mass changes to violet blue indicating the formation of vanadyl oxalate, said vanadyl oxalate being in dilute solution, adding a phosphorous source to the dilute solution of vanadyl oxalate heated over water bath, followed by addition of an aqueous solution of molybdenum source and mixing while adding a Titanium source under stirring, evaporating the solution over water bath till the mass is reduced to about half, further heating the mass till a powder catalyst is obtained.

In an embodiment of the present invention vanadium rich compound is selected from the group consisting of ammonium metavanadate, vanadyl sulphate and oxides of vanadium.

In another embodiment, the oxide of vanadium is vanadium pentoxide.

In another embodiment of the invention the phosphorous source is selected from the group consisting of ortho-phosphoric acid, pyro-phosphoric acid and meta-phosphoric acid.

In yet another embodiment the molybdenum source is ammonium molybdate.

In another embodiment of the invention the titanium source is titanium-pillared clay.

In one embodiment of the invention, the clay is pillared with polyoxymetal cations of titanium and has titania clusters as the pillars between the layers.

In another embodiment of the invention, the clay is selected from a single smectite clay and mixed layer smectite clays.

In another embodiment of the invention, the single smectite clay comprises montmorillonite clay.

In another embodiment of the invention, the mixed layered smectite clay is selected from rectorite and paragonite.

In a further embodiment of the invention, the pillared clay contains one or more rare earth elements selected from cerium, lanthanum and a mixture thereof.

In another embodiment of the invention the ratio of the compounds of vanadium, molybdenum, phosphorous over titanium pillared clay in the catalyst is in a ratio ranging between 1.0: 2.5: 0.5: 20 - 1.0: 30: 1.5: 50.

In a further embodiment of the invention, the pillared clay contains one or more rare earth elements selected from cerium, lanthanum and a mixture thereof.

In still another embodiment of the invention the ratio of the compounds of vanadium, molybdenum, phosphorous over titanium pillared clay in the catalyst is in a ratio ranging between 1.0: 2.5: 0.5: 20 - 1.0: 30: 1.5: 50.

In another embodiment of the invention, the pillared clay contains a homogeneous distribution of pillars in the interlayered spaces thereof forming an array of rectangular openings or pores of a size in the range of 7 to 20 Angstroms high and between 8 and 20 Angstroms wide, enabling the pillared clay to perform like a two-dimensional crystalline molecular sieve.

Detailed description of the invention

The novelty of the present invention lies in providing a catalyst for conversion of 3-picoline to 3-cyanopyridine by reaction of ammonia and air with 3-picoline in a single step, yielding a high purity product, eliminating expensive oxidising agents and enabling the operation of the process on a continuous basis and the inventive step lies in providing non-obvious steps of the process in an environmental friendly manner in comparison to prior art processes.

A preferred pillared clay for use in the catalyst of the invention has been pillared with polyoxymetal cations of titanium and therefore has titania clusters as the pillars between the layers. Besides a single smectite clay such as montmorillonite, mixed layered smectites such as rectorite and paragonite can also be pillared and used in the catalyst of the invention. Examples of pillared clays which possess stability at high temperatures are ones in which the pillars contain one or more rare earth elements such as cerium and/or lanthanum. Such clays are disclosed in U.S. Pat. Nos. 4,753,909 and 4,952,544 and in PCT International Application WO 88/06614, the disclosures of which patents and application are hereby incorporated by reference in their entireties.

It will be understood, however, that pillared clays in which the pillars are substantially free of rare earth elements can be used as a component of the catalyst. Pillared clays and their preparation are described generally in an article entitled "Intercalated Clay Catalysts," Science, Vol. 220, No. 4595, pp. 365-371 (Apr. 22, 1983), the disclosure of which is hereby incorporated by reference in its entirety.

The following examples are given by way of illustration of the present invention and should not be construed to limit the scope of the present invention.

Example 1

Preparation of Ti-Pillared clay: TiO_2- PILC (Titanium pillared clay) was synthesized by pillaring montmorilonite /bentonite clay (sodium ion exchanged) by a solution of partially hydrolysed Ti-polycations. Ti-polycation was prepared by adding the concentrated solution of $TiCl_4$ into 2 moles of HCl(Hydrochloric Acid). The mixture was then diluted by slowly adding water with constant stirring so that final concentration of Titanium in the solution was 0.82 mole and final concentration of HCl was 0.6 mole.

8 g Sodium exchanged clay was dispersed in 2 litre distilled water. The slurry was stirred for 8 h by mechanical stirrer. The Titanium polycation pillaring agent was added to the slurry slowly with vigorous stirring at 90°C. The solution contained 10 m mole titanium/g clay. The resulting solution was further stirred for 4 h. The solution was kept 18 h at room temperature. The mass was filtered under suction and thoroughly washed with distilled water to make chloride ion free. The product is oven dried at 110±10°C for 6 h. Finally it was calcined at 350°C for 12 h in a muffle furnace.

Preparation of Vanadyl oxalate: 45 g vanadium pentoxide in water(1:5) was heated over steam bath and 122 g oxalic acid crystals slowly added pinch wise with stirring till the colour of the slurry changes from yellow to violet blue. It was further heated over steam bath for 15 minutes. Thus the solution of vanadyl oxalate was prepared.

Preparation of the catalyst and its use in ammoxidation of 3-picoline: 6.6 ml vanadyl oxalate solution containing 3.1 g vanadyl oxalate (equivalent to 1.8 g vanadium pentoxide) as prepared above was taken in a porcelain basin. It was diluted with 40 ml of distilled water, mixed thoroughly with stirring and heated at 70-80 °C. To this solution 0.05 g H_3PO_4 (85%) was added and mixed thoroughly. Another solution was made using 0.4 g molybdenum trioxide and 5 ml of (1:1) ammonium hydroxide and heated at 70-80°C. Both the solutions were mixed with stirring at the same temperature. 7.75 g Ti-PILC was added to the mixed solution with constant stirring. It was stirred for another 15 minutes. The mixed mass was heated on a steam bath. This was then heated in an air oven at 110^{0}C for 15 h, then in a muffle furnace for 3 h at 300^{0}C and further at 425^{0}C for 15 h. The powder catalyst was pelletized and used in the form of -6 to +14 BS mesh.

The reaction was carried out using a down flow, fixed bed, pyrex glass reactor of 20 mm i.d.. The reactor is packed with 10 ml (8 g) Ti-PILC based catalyst. The reaction mixture was fed from top of the reactor. 3-Picoline and water in the ratio 1:3 (by vol) was fed at the rate 4.35 ml/h using a syringe pump (Sage instrument). Ammonia gas(2.1 l/h) from gas cylinder and air (4.5 l/h) through calibrated flow meter were fed in to the reactor. The

reaction was carried out at temperature of 425 ± 10^0C and contact time 1.4 s (space velocity 2571 cc/cc cat/h). The product was cooled using ice cooled water and collected at the bottom followed by two number of ice traps. The product was analysed by gas chromatograph using 2 m length carbowax 20 M column at 160^0C temperature and Thermal Conductivity Detector. The yield of the product (3-cyanopyridine) was 80.6% where as the conversion of 3-picoline was 87.6 %

Example 2

Preparation of Ti-Pillared clay: TiO_2- PILC (Titanium pillared clay) was synthesised by pillaring montmorilonite /bentonite clay (sodium ion exchanged) by a solution of partially hydrolysed Ti-polycations. Ti-polycation was prepared by adding the concentrated solution of $TiCl_4$ into 2 moles of HCl(Hydrochloric Acid). The mixture was then diluted by slowly adding water with constant stirring so that final concentration of Titanium in the solution was 0.82 mole and final concentration of HCl was 0.6 mole.

8 g Sodium exchanged clay was dispersed in 2 litre distilled water. The slurry was stirred for 8 h by mechanical stirrer. The Titanium polycation pillaring agent was added to the slurry slowly with vigorous stirring at 90°C. The solution contained 10 m mole titanium/g clay. The resulting solution was further stirred for 4 h. The solution was kept 18 h at room temperature. The mass was filtered under suction and thoroughly washed with distilled water to make Cl^- ion free. The product is oven dried at 110±10°C for 6 h. Finally it was calcined at 350°C for 12 h in a muffle furnace.

Preparation of Vanadyl oxalate: 45 g vanadium pentoxide in water(1:5) was heated over steam bath and 122 g oxalic acid crystals slowly added pinch wise with stirring till the colour of the slurry changes from yellow to violet blue. It was further heated over steam bath for 15 minutes. Thus the solution of vanadyl oxalate was prepared.

8.9 ml vanadyl oxalate solution containing 3.1 g vanadyl oxalate (equivalent to 1.8 g. vanadium pentoxide) was taken in a porcelain basin. It was diluted with 40 ml of distilled water, mixed thoroughly with stirring and heated at 70-80^0C. To this solution 0.1 g H_3PO_4 (85%) was added and mixed. Another solution was made using 0.4 g molybdenum trioxide and 5 ml of (1:1) ammonium hydroxide and heated to 70-80^0C. This solution was added to the first solution with stirring keeping the temperature at about 80^0C. 7.75 g Ti-PILC was added to the mixed solution with constant stirring. It was stirred for another 15 minutes. The mixed mass was evaporated on a steam bath. This was then oven dried at 110-120^0C for 15 h, then calcined in a muffle furnace for 3 h at 300^0C and further at 425^0C for 15 h. The powder catalyst was pelletised and used in the form of -6 to +14 BS mesh.

The reaction was carried out using a down flow fixed bed pyrex glass reactor of 20 mm i.d. The reactor was packed with 5 ml (4.38 g) Ti-PILC based catalyst. The reaction mixture was fed from the top of the reactor 3-picoline and water in the ratio of 1:3 by vol. was fed at the rate of 4.3 ml/h using a syringe pump (Sage instrument). Ammonia gas (2.10 l/h) and air (4.5 l/h) from cylinder through calibrated flow meter were fed into the reactor. The reaction was carried out at temperature 440±10 °C and contact time 0.66 s (space velocity 5438-cc/cc cat/h). The yield obtained was 91% conversion 98.0 %.

Example 3

Preparation of Ti-Pillared clay: TiO_2- PILC (Titanium pillared clay) was synthesised by pillaring montmorilonite /bentonite clay (sodium ion exchanged) by a solution of partially hydrolysed Ti-polycations. Ti-polycation was prepared by adding the concentrated solution of $TiCl_4$ into 2 moles of HCl (Hydrochloric Acid). The mixture was then diluted by slowly adding water with constant stirring so that final concentration of Titanium in the solution was 0.82 mole and final concentration of HCl was 0.6 mole.

8 g Sodium exchanged clay was dispersed in 2 litre distilled water. The slurry was stirred for 8 h by mechanical stirrer. The Titanium polycation pillaring agent was added to the slurry slowly with vigorous stirring at 90°C. The solution contained 10 m mole titanium/g clay. The resulting solution was further stirred for 4 h. The solution was kept 18 h at room temperature. The mass was filtered under suction and thoroughly washed with distilled water to make Cl^- ion free. The product is oven dried at 110±10°C for 6 h. Finally it was calcined at 350°C for 12 h in a muffle furnace.

Preparation of Vanadyl oxalate: 45 g vanadium pentoxide in water(1:5) was heated over steam bath and 122 g oxalic acid crystals slowly added pinch wise with stirring till the colour of the slurry changes from yellow to violet blue. It was further heated over steam bath for 15 minutes. Thus the solution of vanadyl oxalate was prepared.

Solution A was prepared by diluting 18 ml vanadyl oxalate solution containing 9.35 g vanadyl oxalate(equivalent to 5.49 g vanadium pentoxide) with 75 g distilled water and 0.95 g H_3PO_4 (85%) was added and mixed. Solution B was prepared by dissolving 17.6 g ammonium hepta molybdate in 65 g distilled water. Both solutions were heated at 70-80 °C, solution A was added to solution B and 10.5 g Ti-pillared clay was added and mixed thoroughly. This mixed mass was then heated over steam bath till the mass reduced to about half. Semi dried mass of the catalyst was then oven dried at 110-120 °C for 15 h and then calcined at 300 °C for 3 hours and further at 400-425 °C for 15 h. This was then pelletised (6 mm dia) and sized to -6+14 mesh size.

The reaction was carried out using a down flow, fixed bed, pyrex glass reactor of 20 mm I.D. The reactor was packed with 8.8 ml (13.2 g) Ti-PILC based catalyst. The reaction mixtures, 3-Picoline and water in the ratio 1:3 (by vol.) was fed at the rate 6.0 ml/h using a syringe pump (sage instrument). Ammonia gas (2.4 l/h) from gas cylinder and air (4.5 l/h) through calibrated flow meter were fed in to the reactor. The reaction was carried out at temperature of 430 ± 10^0C and contact time 1.05. The product was cooled using ice cooled water and collected at the bottom followed by two number of ice traps. The product was analysed by gas chromatograph using 2 m length carbowax 20 M column at 160^0C temperature and Thermal Conductivity Detector. The yield of 3- cyanopyridine obtained was 93.0 % the conversion 96.1 %.

The main advantages of the present invention are:

1. The catalyst is prepared in aqueous medium.
2. The said catalyst is active, stable and low cost material.

We claim:

1. A pillared clay based vanadia catalyst useful for the conversion of 3-picoline to 3-cyanopyridine, said catalyst comprising vanadium, phosphorous and molybdenum on a Ti-pillared clay support.
2. A catalyst as claimed in claim 1 wherein the clay is pillared with polyoxymetal cations of titanium and has titania clusters as the pillars between the layers.
3. A catalyst as claimed in claim 1 wherein the clay is selected from a single smectite clay and mixed layer smectite clays.
4. A catalyst as claimed in claim 3 wherein the single smectite clay comprises montmorillonite clay.
5. A catalyst as claimed in claim 3 wherein the mixed layered smectite clay is selected from rectorite and paragonite.
6. A catalyst as claimed in claim 1 wherein the pillared clay contains one or more rare earth elements selected from cerium, lanthanum and a mixture thereof.
7. A catalyst as claimed in claim 1 wherein the ratio of the compounds of vanadium, molybdenum, phosphorous over titanium pillared clay in the catalyst is in a ratio ranging between 1.0: 2.5: 0.5: 20 - 1.0: 30: 1.5: 50.
8. A catalyst as claimed in claim 1 wherein the pillared clay contains a homogeneous distribution of pillars in the interlayered spaces thereof forming an array of rectangular openings or pores of a size in the range of 7 to 20 Angstroms high and between 8 and 20 Angstroms wide, enabling the pillared clay to perform like a two-dimensional crystalline molecular sieve.
9. A process for the preparation of a pillared clay based vandia catalyst comprising first preparing vanadyl oxalate by heating a vanadium rich compound on a water bath followed by addition of oxalic acid till the colour of the mass changes to violet blue indicating the formation of vanadyl oxalate, said vanadyl oxalate being in dilute solution, adding a phosphorous source to the dilute solution of vanadyl oxalate heated over water bath, followed by addition of an aqueous solution of molybdenum source and mixing while adding a Titanium source under stirring, evaporating the solution over water bath till the mass is reduced to about half, further heating the mass till a powder catalyst is obtained.
10. A process as claimed in claim 9 wherein the vanadium rich compound is selected from the group consisting of ammonium metavanadate, vanadyl sulphate and oxides of vanadium.

11. A process as claimed in claim 10 wherein the oxide of vanadium is vanadium pentoxide.
12. A process as claimed in claim 9 wherein the phosphorous source is selected from the group consisting of ortho-phosphoric acid, pyro-phosphoric acid and meta-phosphoric acid.
13. A process as claimed in claim 9 wherein the molybdenum source is ammonium molybdate.
14. A process as claimed in claim 9 wherein the titanium source is titanium-pillared clay.
15. A process as claimed in claim 14 wherein the clay is pillared with polyoxymetal cations of titanium and has titania clusters as the pillars between the layers.
16. A process as claimed in claim 14 wherein the clay is selected from a single smectite clay and mixed layer smectite clays.
17. A process as claimed in claim 16 wherein the single smectite clay comprises montmorillonite clay.
18. A process as claimed in claim 16 wherein the mixed layered smectite clay is selected from rectorite and paragonite.
19. A process as claimed in claim 14 wherein the pillared clay contains one or more rare earth elements selected from cerium, lanthanum and a mixture thereof.
20. A process as claimed in claim 9 wherein the ratio of the compounds of vanadium, molybdenum, phosphorous over titanium pillared clay in the catalyst is in a ratio ranging between 1.0: 2.5: 0.5: 20 - 1.0: 30: 1.5: 50.
21. A process as claimed in claim 9 wherein the reaction is carried out at a space velocitie in the range of 1500 to 5500 h^{-1} and after dilution of the catalyst with an inert medium to a range in the extent of 0.5 to 4 by volume with respect to the volume of catalyst.
22. A process as claimed in claim 9 wherein the reduced mass is heated at a temperature of about 110^0C in an air oven for 15 hours and then further heated in a muffle furnace at a temperature of about 300^0C for 3 hours and subsequently at a temperature of about 425^0C for 15 hours.
23. A process as claimed in claim 9 wherein the catalyst powder obtained is pelletized and sized to -6 to +14 mesh size.
24. A process as claimed in claim 9 wherein the vanadium rich compound comprises vanadium pentoxide, said process comprising heating vanadium pentoxide with water in the range of 1:3 to 1:5 (w/v) followed by addition of oxalic acid in the range of 2.5 to 3.0 parts by weight of vanadium pentoxide till the colour of the mass changes to violet blue; adding phosphorous source to the dilute solution of vanadyl oxalate in the range of 2 to 4

times by volume of vanadyl oxalate over heating bath at a temperature in the range of 70 to 80°C; preparing aqueous solution of molybdenum source in the range of 1:4 to 1:6 (w/v) and heating over a heating bath at a temperature in the range of 70 to 80°C; mixing both the solutions in heating condition over heating bath with appropriate amount of titanium-pillared clay under stirring; evaporating the mixture over a heating bath till the mass reduces to half; heating the mass in an air oven at a temperature in the range of 100 to 120°C for a time period in the range of 10 to 16 hours and in a muffle furnace at a temperature in the range of 250 to 350°C for a time period in the range of 16 to 20 hours and pelletizing the same size range of -6 to +14 BSS.

25. A process for the conversion of 3-picoline into 3-cyanopyridine in a single step, said process comprising reacting 3-picoline, ammonia and air in the presence of a Ti-pillared clay based vanadia catalyst to obtain 3-cyanopyridine, without requiring addition of oxidizing agents.

26. A process as claimed in claim 25 wherein the clay is pillared with polyoxymetal cations of titanium and has titania clusters as the pillars between the layers.

27. A process as claimed in claim 26 wherein the clay is selected from a single smectite clay and mixed layer smectite clays.

28. A process as claimed in claim 27 wherein the single smectite clay comprises montmorillonite clay.

29. A process as claimed in claim 27 wherein the mixed layered smectite clay is selected from rectorite and paragonite.

30. A process as claimed in claim 27 wherein the pillared clay contains one or more rare earth elements selected from cerium, lanthanum and a mixture thereof.

31. A process as claimed in claim 26 wherein the ratio of the compounds of vanadium, molybdenum, phosphorous over titanium pillared clay in the catalyst is in a ratio ranging between 1.0: 2.5: 0.5: 20 - 1.0: 30: 1.5: 50.

32. A process as claimed in claim 26 wherein the pillared clay contains a homogeneous distribution of pillars in the interlayered spaces thereof forming an array of rectangular openings or pores of a size in the range of 7 to 20 Angstroms high and between 8 and 20 Angstroms wide, enabling the pillared clay to perform like a two-dimensional crystalline molecular sieve.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B01J C07D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal, COMPENDEX, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3 970 659 A (ELION GLENN R ET AL) 20 July 1976 (1976-07-20) the whole document ---	
A	US 6 475 944 B1 (CHAE HO-JEONG ET AL) 5 November 2002 (2002-11-05) the whole document ---	
A	US 3 981 879 A (ELION GLENN R ET AL) 21 September 1976 (1976-09-21) the whole document ---	
A	US 2 861 999 A (D ALESSANDRO ALFRED F) 25 November 1958 (1958-11-25) the whole document --- -/--	

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
10 February 2004	18/02/2004

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INTERNATIONAL SEARCH REPORT

International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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